[Translation]

(19) Japan Patent Office (JP)

(12) PATENT ISSUANCE REPORT

(11) Patent Application Release No.
Patent Release Hei. 6-244172

(43)Release date: September 2, 1994

(51) Int.Cl.[5]	Identification Symbol		Office Control No.	FI	Technology Indicators
H 01 L 21/312		M	7352-4M		
		B	7352-4M		
21/90		S	7514-4M		
H 05 K 3/46		Z	6921-4E		
		E	6921-4E		

Examination requested: Not yet
No. of Items in Application: 2 OL (Total 5 pages)

(21) Application No.: Patent Application Hei.5-28985

(22) Application date: February 18, 1993

(71) Applicant: 000003159
Toray Industries, Inc.
2-1 Muromachi 2-chome
Chuo-ku, Tokyo [Japan]

(72) Inventor: Katsuhiro Tanba
c/o Toray Industries. Shiga Office
1-1 Sonoyama 1-chome
Otsu-shi, Shiga Prefecture [Japan]

(72) Inventor: Masaya Asano
[same address]

(54) **Name of Invention:** Multi-layered Wiring Configuration

(57) **Summary**

Makeup: In multi-layered wiring equipped with

- a first metal wiring formed on a base,
- a first layer of polyimide dielectric film covering said first metal wiring layer
- and a second layer of metal wiring connected to above-noted first layer of metal wiring via an opening formed in said first layer's polyimide dielectric film, all as the minimal component unit

this invention bears on multi-layered wiring configurations characterized by having a hexamethyldisilazane coating film installed between the metal wiring and the polyimide dielectric film formed on said metal wiring.

Effects: With this invention no corrosion of the wiring conductors occurs and reactions between such metals as copper and nickel and the polyimide film can be prevented, so that the polyimide's heat resistance is improved, making it safer operationally and enabling the manufacture of multi-layered wiring configurations with high reliability.

Scope of patent Application

Application Item 1: A multi-layered wiring configuration which is characterized--in multi-layered wiring having a first metal wiring formed on a base, a first layer of polyimide dielectric film covering said first metal wiring layer and a second layer of metal wiring connected to above-noted first layer of metal wiring via an opening formed in said first layer's polyimide dielectric film, all being the minimal component unit--by having installed a hexamethyldisilazane covering film between the metal wiring and the polyimide dielectric film formed on said metal wiring.

Application Item 2: The multi-layered wiring configuration described in Application item 1, which is characterized by the metal wiring being copper wiring.

Detailed Explanation of Invention

0001 Field for Commercial Utilization: This invention is one relating to multi-layered wiring, and more specifically bears on multi-layered wiring configurations for high-density mounting.

0002 Usual Technology: For multi-layered wiring configurations in high-density mountings that use polyimide resin as the interlayer dielectric film, copper/polyimide multi-layered wiring configurations are generally known which use copper for the metal wiring (E.g., *Nikkei Electronics* 8/27/84, pp. 145-158). However, when such metals as copper or nickel are used as the wiring metals, the problem has existed that the heat resistance of the polyimide is reduced. (For instance, in Saiki, et al, Papers of 1975 National Convention of Electronic Communications Soc., pp. 378, 380; Miura, et al., Monographs C of Electronic Data

Communications Soc., vol. J71-C No. 11, pp. 1510-1515, Nov., 1988.) Therein, with copper, the method generally applied is to put a thin chrome film in the interface of copper with the polyimide. Or, the method has been devised of putting a chromate-processed coating at the interface between the copper and the polyimide layer. (Patent Release Hei.4[1992]-39990)

0003 **Problems the Invention Seeks to Resolve:** Still, such usual methods have had such shortcomings as wiring conductors being corroded by voltaic effects arising locally between the disparate metals, the heat resistance of the polyimide being reduced because of reactions at the interface of the metal wiring and the polyimide resin film, and operational safety problems.

0004 This invention is one devised after studying the deficiencies of the existing technology, and is given the purpose of providing highly reliable multi-layered wiring configurations which, by preventing corrosion of wiring conductors and reactions between metal wiring and polyamide dielectric film, improve the polyimide's heat resistance and so can secure its operating safety.

0005 **Means to Resolve the Problems:** This invention's purpose is attained by multi-layered wiring configurations --in a multi-layered wiring configuration equipped with a first metal wiring layer formed on a base, a first polyimide dielectric film covering said first wiring layer and a second wiring layer connected to the above-noted first wiring layer via an opening formed in said first polyimide film as the minimal component unit—characterized by having a hexamethylsilazane coating film between the metal wiring and the polyimide insulating film formed on said metal wiring. When the metal wiring is copper, the effects attained are particularly marked.

0006 The multi-layered wiring configuration of this invention is equipped--as a minimal component unit--with a first metal wiring layer formed on a substrate, a polyimide dielectric film covering said first metal wiring layer and a second metal wiring layer connected to above-noted first metal wiring layer by an opening made in said first polyimide dielectric film. This minimal component unit is a configuration of two layers of wiring. I.e., a three-layered wiring configuration would have a second polyimide dielectric film formed on the second metal wiring layer and a third layer of metal wiring formed on top of that, in

that order; while a multiple wiring configuration would have repetitions of the same made up.

0007 Silicon, aluminum, ceramics, sapphire, etc., are used for the substrate in this invention; but it is not limited to these.

0008 For the metal wiring in this invention, copper, nickel and/or copper alloys and nickel alloys are used alone or in combined layers with such electrically conductive materials as aluminum, gold, chrome and platinum to give the desired capabilities, and are used in layers that are patterned or formed over the entire surface.

0009 This invention is typified by putting a hexamethyldisilazane film between the metal wiring and the polyimide dielectric film formed on said metal wiring. Here, what is called a hexamethyldisilazane coating is a film consisting mainly of hexamethyldisilazane.

0010 Hexamethyldisilazane is a compound expressed by formula (1).

$$(CH_3)_3\ Si\text{-}NH\text{-}Si(Ch_3)_3 \qquad (1)$$

0011 The hexamethyldisilazane in the hexamethyldisilazane in this invention is not limited to a perfectly structured hexamethyldisilazane, but may also be a compound in which part of the hexamethyldisilazane structure has been heat decomposed, such as when the polyimide dielectric film is heat cured.

0012 Also, a substance other than hexamethyldisilazane may be used within a scope that does not interfere with the effects of this invention. Specifically, we can mention tetraethoxysilane, methyltriethoxysilane, dimethyl-dioxysilane, silicon hydroxide, methanol, ethanol, isopropanol, water, etc.

0013 The method for making hexamethyldisilazane coating is not particularly delimited; but we can mention such coating methods as spin-coating or deep coating. When doing the coating, it is desirable to use undiluted hexamethyldisilazane, although one may also use it diluted with a solvent. For the solvent, such substances as methanol, ethanol and isopropanol may be used.

0014 There is no specific limitation on the thickness of the hexamethyldisilazane coating; but 0.005~1μm is desirable, with 0.01~0.1μm being even better.

0015 To further improve the effects of this invention, it is desirable to put a hexamethyldisilazane coating similarly between the metal wiring and the polyimide dielectric film formed under said metal wiring.

0016 The polyimide dielectric film in this invention can be obtained by first selectively combining a dianhydride of tetracarbonic acid with a diamine and cause these to react in a polar solution such as N-methyl-2-pyrrolidone, N, N-dimethylacetoamide or the like to make a polyimide precursor of varnish, and then to apply this polyimide precursor of varnish to the substrate and heat it in the range of 200~400°C to get the polyimide after drying and shrinking, using well-known methods. It is desirable that such specific examples of varnish's polyimide precursors be used as dianhydric pyrromellitic acid and 4,4⁻diaminodiphenylether, 3,3⁻, dianhydrous 4,4⁻ benzophenontetracarbonic acid and 4,4⁻diaminodiphenylether, dianhydrous 3, 3⁻, 4,4⁻ biphenyltetracarbonic acid and dianhydrous 4,4-diaminodiphenylether, dianhydrous pyrromellitic acid and 3,3⁻ (or 4, 4⁻)-diaminodiphenylsulfhone, dianhydrous pyrromellitic acid and dianhydrous 3,3⁻, 4,4⁻-benzophenontetracarbonic acid and dianhydrous 3,3⁻ (or 4,4⁻)-diaminodiphenylsulfone, dianhydrous 3,3⁻, 4,4⁻-benzophenontetracarbonic acid and 3,3⁻ (or 4,4⁻)-diaminodiphenylsulfone, dianhydrous 3,3⁻, 4,4⁻ biphenyltetracarbonic acid and 3,3⁻ (or 4,4⁻)-diaminodiphenylsulfone, dianhydrous pyrromellitic acid and 4,4⁻ diaminodiphenyl-sulfide, dianhydrous 3,3⁻, 4,4⁻-benzophenontetracarbonic acid and 4,4⁻-diaminodiphenylsulfide, dianhydrous 3,3⁻, 4,4⁻-biphenyltetracarbonic acid and 4,4⁻ diaminodiphenylsulphide, dianhydrous 3,3⁻ 4,4⁻benzophenontetracarbonic acid and paraphenylene-diamine, dianhydrous 3,3⁻, 4,4⁻biphenyltetracarbonic acid and paraphenylene-diamine, dianhydrous pyrromellitic acid and dianhydrous 3, 3⁻, 4,4⁻-benzophenontetracarbonic acid and paraphenylene-diamin, dianhydrous pyrromellitic acid and dianhydrous 3,3⁻, 4,4⁻-biphenyltetracarbonic acid and paraphenylene-diamine, dianhydrous 3,3⁻, 4,4⁻-diphenylethertetracarbonic acid and 4,4⁻diaminodiphenylether, dianhydrous 3,3⁻, 4,4⁻-diphenylethertetracarbonic acid and paraphenylene-diamine, dianhydrous pyrromellitic acid and 4,4⁻diaminodiphenylether and bis-3-aminopropyl)tetramethyldisiloxane.

0017 To devise a connection with the upper metal wiring, the polyimide dielectric film will be patterned to make an opening in it.

0018 Consequently, the polyimide precursor is made photosensitive so that it can be direct-patterned and the processes can be simplified. Methods for making it photosensitive are described, for instance, in Patent Releases 55-30207 and 53-127723.

0019 Next, we will explain an example of the manufacturing method for this invention's multi-layered wiring configuration.

0020 One makes, for example, the first metal wiring layer to include the grounding layer and power source on an alumina-ceramic substrate. The metal wiring is made, for instance, 0.3µm thick by sputtering onto the substrate. After forming another 10µm by electroplating, one does photo-etching to obtain a desired wiring pattern. One next forms first wiring layer by spin-coating undiluted hexamethyldisilazane to form the coating of that substance.

0021 Next, one forms the first polyimide dielectric film on this substrate. Usually, to make an opening (connecting hole) to the upper wiring, said polyimide dielecric film is patterned, which can be done by several methods.

0022 When using a polyimide precursor with photosensitivity, after it is applied and dried a mask is placed on the photosensitive polyimide precursor and it is subjected to ultraviolet light. Then it is developed. After that, it is heated to get the polyimide dielectric film. When using a polyimide precursor without photosensitivity, it is applied, dried and heated, after which—with a thin metal film or silicon oxide as a mask—the polyimide can be etched with an oxygen plasma to form the pattern. The drying is best done at 70~160°C. The heat processing is done from five minutes up to five hours in a nitrogen atmosphere, choosing a temperature range from room temperature up to 450°C and raising the temperature in stages or raising it continuously in that temperature range. The maximum temperatures for this heat treatment are 120~450°C, but preferably 130~450°C. E.g., one may heat for 30 minutes each at 130°C, 200°C and 400°C, or raise the temperature linearly over two hours from room temperature to 400°C.

0023 It is desirable that the hexamethyldisilazane coating with an opening (connecting hole) to the upper wiring have its surface etched by a solution of persulfuric ammonium or by a plasma.

0024 Next, one forms on the wiring substrate the second wiring layer obtained in this way. Just like the first layer of wiring, the wiring is formed by sputtering copper on the substrate up to 0.3μm thick; and after adding another 10μm by electroplating, one uses photo-etching to get a two-layered wiring configuration.

0025 Proceeding in the same way, one forms a coating of hexamethyldisilazane by spin-coating on the second wiring layer pattern, goes on to form the polyimide dielectric film on that and then form the wiring pattern of the third layer to get a triple-layered wiring configuration. By repeating these processes the necessary number of times, a wiring configuration of even more layers can be yielded.

0026 **Application Examples:** Below, we will explain the specifics of this invention with the application examples; but this invention is not limited to these.

0027 **Application Example 1, Comparative Example 1:** We synthesized polyimide precursor (A) by causing a reaction over four hours at 50°C in a concentrated 15% solution of N-methyl-2-pyrrolidone among dianhydrous 3,3',4,4'-benzophenontetracarbonic acid (1 mol), 4,4'-diaminodiphenylether (0.95 mol) and bis(3-aminopropyl)tetramethyldisilazane (0.05 mol).

0028 Copper was sputtered on the silicon substrate to 0.3μm with 5μm added by electroplating, an undiluted solution of hexamethyldisilazane was spin-coated on half the substrate to form a hexamethyldisilazane coating about 0.05μm thick to make up half with hexamethyldisilazane coating (Application Example 1) and half without it (Comparative Example 1).

0029 We applied polyimide precursor (A) to this substrate and dried it in a nitrogen atmosphere at 80°C for 60 minutes to form a polyimide precursor film 10μm thick. We soaked the substrate with this polyimide precursor coating in a solution of N-methyl-2-pyrrolidone, dissolving the polyimide precursor coating. After rinsing it with

2-propanol, we blow-dried it in nitrogen. Then, after soaking the substrate for one minute in a 10% solution of persulfuric ammonium, we washed and dried it.

0030 The result was that the part on which a hexamethyldisilazane coating was formed had no remaining film and had a resistance value of under 1Ω; but the part on which no hexamethyldisilazane coating was formed remained insoluble in the solution and showed a high resistance of 10 megaΩ or more.

0031 Clearly, then, a reaction had occurred at polyimide precursor/copper interface and had created insoluble reaction products in the solution.

0032 From these results we know that by forming a hexamethyldisilazane coating on the copper we can prevent reactions at the interface of the polyimide precursor and the copper.

0033 **Application Example 2, Comparative Example 2:** We caused dianydrous 3,3⁻, 4,4⁻-benzophenoncarbonic acid (1mol[? Text too faint to read.] and dianhydrous [text too faint to read] (0.5mol) to react for 4 hours at 60°C in a 16% concentration solution of N-methyl-2-pyrrolidone to synthesize polyimide precursor (B).

0034 We formed a copper film of 0.3μm on the silicon substrate by sputtering, formed another 5μm by electroplating and then spin-coated undiluted hexamethyldisilazane to form a substrate with a hexamethyldisilazane coating of about 0.05μm (Application Example 2) and a substrate without it (Comparative Example 2).

0035 We applied polyimide precursor (B) to these substrates and heated them in a nitrogen atmosphere for 30 minutes each at 130°C, 200°C and 400°C to form polyimide dielectric film of 10μm. We scaled off part of the polyimide dielectric film and copper from these substrates, etched off the copper with a 10% solution of persulfuric ammonium, leaving just the polyimide dielectric films. After washing in water, we dried them for 30 minutes at 200°C to make samples for measuring heat resistance.

0036 Now, on the silicon substrate with no copper on it (the silicon substrate on which the heat resistance of the

polyimide does not drop) we formed a polyimide dielectric film 10μm thick; and we made a sample with the polyimide dielectric film scaled off the substrate to be a reference sample.

0037 Measurements of the polyimide's heat resistance were done using a Shimazu Works (Ltd.) TCA30 (thermobalance) in a helium atmosphere with a sample of 20mg while raising the temperature 10°C/min. We checked temperatures when there was a 5% reduction in the amount and made those the temperatures expressing heat resistance.

0038 The result for Application Example 2 was 525°C, for Comparative Example 2 was 420°C and for the reference sample was 525°C. This showed us that forming a hexamethyldisilazane coating on the copper keeps the polyimide's heat resistance from dropping.

0039 **Application Example 3, Comparative Example 3:** After sputtering 0.5μm of nickel on the silicon substrate, we made a substrate on which we had spin-coated about 0.05μm of undiluted hexamethyldisilazane (Application Example 3) and a substrate without that (Comparative Sample 3).

0040 Onto these substrates we applied polyimide precursor (B) and heated them in a nitrogen atmosphere for 30 minutes each at 130°C, 200°C and 400°C to form 10μm thick polyimide dielectric films. We scaled the polyimide dielectric films from the substrates and made them test samples for heat-resistance measurements.

0041 Our measurements of the polyimide's heat resistance were done just as with Application Example 2.

0042 The results were 525°C for Application Example 3, 450°C for the comparative example and 525°C for the reference sample. From this we found that by applying the hexamethyldisilazane coating on the nickel, we kept the heat resistance of the polyimide from dropping.

0043 **Application Example 4, Comparative Example 4:** We mixed together 348g of Application Example 1's polyimide precursor (A), 31g of dimethylaminoethylmetacrylate and 2.6g of Michler's ketone dissolved in a solution of 31g of N-methyl-2-pyrrolidone to synthesize photosensitive polyimide precursor (C).

0044 We used sputtering to form 0.3μm of copper on a 99.5% aluminum-ceramic substrate; and, after electroplating another 10μm, we did photo-etching to form the wiring pattern. On half of the substrate we spin-coated undiluted hexamethyldisilazane to make a coating of hexamethyldisilazane about 0.05μm thick on that half (Application Example 4) and the other half without that coating (Comparative Example 4).

0045 We applied photosensitive polyimide precursor (C) onto the substrate, dried it for 120 minutes at 80°C in a nitrogen atmosphere to form a 20μm film of photosensitive polymide precursor. Using Canon (Inc.) ultraviolet exposure meter PLA-501F, we exposed the substrate to 300mJ/cm^2 through a mask. We then immersed and developed it in a developing solution of N-methyl-2-pyrrolidone at 70% by weight and methanol at 30% by weight while applying ultrasound, rinsed it with 2-propanol and blow-dried it in nitrogen to form an opening in the photosensitive polyimide precursor coating matching the metal wiring pattern. Next, we heated it in a nitrogen atmosphere for 30 minutes each at 130°C, 200°C and 400°C to form a polyimide dielectric film 20μm thick.

0046 With Application Example 4, in order to remove the hexamethyldisilane coating at the opening, we etched for one minute in a 10% persulfuric ammonium solution, washed it and dried it.

0047 Next, we sputtered 0.3μm of copper, electroplated another 10μm and then used photo-etching to form the second layer wiring pattern and get a dual-layer wiring configuration.

0048 When we checked conduction in the first-layer and second-layer metal wiring of this two-layered wiring configuration, the part with the hexa-methyldisilazane coating on it had good conduction; but conduction in the part without the hexamethyldisilazane was poor.

0049 From these findings, we found that by coating the copper with hexamethyldisilazane, we obtained reliable connections (conduction) for the metal wiring.

0050 By using this invention, one can eliminate corrosion of the wire conductors and prevent a polyimide dielectric film's reactions with such metals as copper, nickel, etc., and so improve the polyimide's heat resistance and secure its safe operation, so that one can fabricate multi-layered wiring configurations of high reliability.